

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )  
Takanori SHINOKI et al. )  
Serial No.: 09/529,255 )  
Filed: April 11, 2000 )  
SUPPORT MEMBER FOR )  
SEMIPERMEABLE MEMBRANE )

Group Art Unit:1771  
Examiner: John J. Guarriello

DECLARATION PURSUANT TO 37 C.F.R. §1.132

Honorable Commissioner of Patents and Trademarks  
Alexandria, VA 22313-1450

Sir:

I, Takanori SHINOKI, declare that:

1. I am one of the co-inventors of the invention disclosed and claimed in the application identified in caption.

2. I currently reside at 2-34 Uguisudai Kawanishi-Shi, Hyogo-Ken, 666-0133 Japan.

3. I graduated the engineering department of Kyoto University, Master course of Fiber Chemistry on March 31, 1960.

4. I have been employed since May 1, 1995 by Miki Tokusyu Paper MFG. Co., Ltd., the assignee of the present application, and have been engaged in research and development of new product until the present.

5. I conducted the experiments in order to show the advantages or unexpected results of the present invention in comparison with the invention set forth in the cited reference U.S.P. No. 4,795,559 of Ietsugu Shinjou et al., I conducted the experiments represented by Experiment Examples and prepared the data in attached Exhibit A.

6. It is declared by the undersigned that all statements

made herein of undersigned's own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonments, or both, under 18 U.S. Code 1001 and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Dated this

day of November, 2004

Takanori Shinoki  
Takanori SHINOKI

## Exhibit A

[Technical point]

The salt concentration of seawater is generally 3.5% (osmotic pressure: about 25 kg/cm<sup>2</sup>) in the adjacent seas of Japan. It is necessary to apply an additional pressure of 20 kg/cm<sup>2</sup> or more (a total of 45 kg/cm<sup>2</sup> or more) to operate an ultrapure water production facility safely for seawater desalination. It is necessary to apply a further higher pressure of about 90 to 100 kg/cm<sup>2</sup> for obtaining a desalted water yield of close to 60%.

Such facilities are often operated intermittently, and backpressure is inevitably generated when the operation is halted (so-called "reflux" phenomenon). The backpressure becomes larger when the filtration is conducted under higher pressure. The bond strength between the support and the semipermeable resin membrane is desirably higher for prevention of the filter destruction by backpressure peeling. In other words, the bond strength is a quite important property for consistent continuous operation of such facilities.

The object of this report is to make clearer the difference in effects between the present invention and the cited reference invention by determining the bonding strengths between the support and the semipermeable resin membrane respectively of the present and reference inventions.

[Experiment Example]

[Preparation of nonwoven fabric A (present invention)]

A mixture of 60 parts by weight of a drawn polyethylene

terephthalate (PET) fiber having a fiber fineness of 1.3 denier, a double refraction ( $\Delta n$ ) of 0.192, a heat shrinkage stress (200°C) of 0.28 g/d, and a fiber length of 5 mm, and 40 parts by weight of an undrawn PET fiber (as binder fiber) having a fiber fineness of 1.1 denier, a  $\Delta n$  of 0.012, and a fiber length of 5 mm was blended well and dispersed in water, to give an aqueous slurry at a fiber concentration of 0.05%. Then, the slurry was sheeted in a cylinder Yankee paper machine by common method to give a sheeted web.

The sheeted web was then calendered by common method in a heat-calendering machine having a pair of metal and cotton rolls under the condition of a metal-roll setting temperature of 230°C, a linear pressure of 80 kg/cm, and a processing speed of 10 m/min, while bringing the non-contact face of the web during sheeting in the Yankee machine into contact with the metal roll (hereinafter, this face is referred to as "top" face).

Subsequently, the rear face of the resulting web was calendered by bringing the rear face into contact with the metal roll (hereinafter, this face is referred to as "bottom" face), to give double-face calendered nonwoven fabric A. The properties thereof were summarized in Table 1.

[Preparation of nonwoven fabric B (cited reference invention)]

Nonwoven fabric B of the cited reference (U.S.P. No. 4,795,553) was prepared in a manner as close to the method described in "Example 1" of the cited reference as possible. The PET fiber used was a commercially available product manufactured by Kuraray Co., Ltd.

<Preparation of wet nonwoven fabric>

50% of a drawn PET staple fiber having a fiber fineness of 1.3 denier, a double refraction ( $\Delta n$ ) of 0.18, a heat shrinkage stress (200°C) of 0.05 g/d, and a fiber length of 5 mm and 50% of an undrawn PET fiber having a fiber fineness of 1.0 denier a double refraction ( $\Delta n$ ) of a double refraction ( $\Delta n$ ) of 0.011, a heat shrinkage stress (200°C) of 0.01 g/d), and a fiber length of 5 mm were sheeted by common wet method, to give a wet web having a high density of about 38 g/m<sup>2</sup>.

<Preparation of dry nonwoven fabric>

A mixture containing a drawn PET fiber having a fiber fineness of 2.0 denier a double refraction ( $\Delta n$ ) of 0.18, a heat shrinkage stress (200°C) of 0.05 g/d) and a fiber length of 51 mm at 65% and an undrawn PET binder fiber having a fiber fineness of 2.0 denier a double refraction ( $\Delta n$ ) of 0.011, a heat shrinkage stress (200°C) of 0.01 g/d) and a fiber length of 38 mm at 35% was blended, opened, and sheeted in a crosslayer machine into a web with the fiber oriented in the transverse direction. The resulting web having a basis weight of 38 g/m<sup>2</sup> was subjected slightly to water needling, to connect the fibers temporarily.

<Bonding two nonwoven fabrics>

The wet and dry nonwoven fabrics were laminated, and the dry nonwoven fabric face of the laminated fabric and then the wet-laid face thereof were brought into contact with a metal roll and processed under the condition of a temperature of 215°C and a linear pressure of 30 kg/cm. Properties of the bonded nonwoven fabric (nonwoven fabric B) thus obtained are summarized in Table 1.

[Physical properties]

(1) Basic properties of nonwoven fabrics

Table 1

		Nonwoven fabric A (present invention)	Bonded nonwoven fabric B (reference invention)
Basis weight (g/m <sup>2</sup> )		79.3	83.2
Thickness (mm)		0.095	0.113
Density (g/cm <sup>3</sup> )		0.83	0.74
Tensile strength (kgf/15mm)	MD	16.3	12.3
	CD	2.43	2.92
Elongation (%)	MD	12.1	13.9
	CD	16.8	16.4
Mean value of breaking length at an elongation of 5% (km)		5.7	3.4
Air permeability (cc/cm <sup>2</sup> /sec)		1.86	1.98

(Note) MD: machine direction, CD: crosswise direction

(2) Pore diameter and pore-diameter distribution of nonwoven fabrics

a) The pore diameter of nonwoven fabrics was determined by using "Perm Porometer" manufactured by Porous Materials, Inc., according to the method specified in JIS K3832 (1990, bubble point method). Results are summarized in Table 2.

Table 2

	Nonwoven fabric A (present invention)	Nonwoven fabric B (reference invention)
Minimum pore diameter (μm)	0.11	2.01
Mean porosity (μm)	2.90	11.31
Maximum pore diameter (μm)	31.2	44.3

Although there seems to be no significant difference in the maximum pore diameter between nonwoven fabrics A and B, note that there is a distinct difference in frequency. It is

apparent in the following micropore distribution curves.

b) Micropore distribution curve

The micropore distribution curves of the nonwoven fabrics A and B are shown here to make Table 2 clearer.

<Figure 1> Micropore distribution (differential) curve of nonwoven fabric A.

<Figure 2> Micropore distribution (histogram) of nonwoven fabric A.

<Figure 3> Micropore distribution (differential) curve of nonwoven fabric B.

<Figure 4> Micropore distribution (histogram) nonwoven fabric B.

The pore-diameter distribution curves shown in Fig.1 to Fig. 4 are to reinforce the pore diameter data described in "Table 5" of the present specification (Application No. 09/529,255), confirming that the pores in nonwoven fabric A are finer and more uniformly distributed than those in nonwoven fabric B although the air permeability data of these fabrics are almost the same.

(3) Determination of the bonding strength of semipermeable resin membrane

<Preparation of semipermeable resin membrane>

A mixture of 17 parts by weight of polysulfone (product name: Ultrason S, manufactured by BASF), 80 parts by weight of N-methyl-2-pyrrolidone, and 3 parts by weight of formalin was stirred at 50°C for 6 hours under heat, to give a semipermeable

resin membrane solution for coating.

<Coating semipermeable resin membrane>

The resin membrane solution was coated on the top face of nonwoven fabric A and on the low-density layer (wet nonwoven fabric) face of nonwoven fabric B at room temperature to a final film thickness of 60  $\mu\text{m}$ . After allowing the resin solution to penetrate sufficiently into the support for 10 seconds, the nonwoven fabric was immersed in a water bath, causing coagulation. The fabric was left in water for 5 hours, during which water was fed into the water bath so that the nonwoven fabric surface became into contact with fresh water.

After water washing, each nonwoven fabric was then dried in a hot-air dryer at 60°C for 12 hours, to give a semipermeable resin membrane-coated sample. The thickness of the membrane formed was about 60  $\mu\text{m}$  on each nonwoven fabric.

<Determination of membrane-bonding strength>

The resin-coated "nonwoven fabric A" and "nonwoven fabric B" thus obtained were cut into pieces of 15 mm in width, and the membrane-bonding strength thereof was determined according to the method specified in JIS P8139 (B method). Results are summarized in Table 3.

Table 3

	Nonwoven fabric A (present invention)	Nonwoven fabric B (cited reference invention)
Membrane-bonding strength (g/15mm)	54	13
Resin penetration	Absence	Presence

(Note) Presence or absence of penetration was determined by visual observation.



The membrane-bonding strength of nonwoven fabric A of the present invention is four times larger than that of nonwoven fabric B of the cited reference invention, indicating that fabric A is highly resistant to back pressure. The fact that nonwoven fabric A has an air permeability almost identical with that of nonwoven fabric B even though fabric A has finer pores indicates that nonwoven fabric A contains a great number of uniform and fine pores as described in the specification of the present invention. This is the most advantageous feature of the present invention.

In addition, as described in the specification, presence of larger pores in support leads to penetration of resin. If penetrated, the resin inevitably causes some shrinkage in volume during wet coagulation, leading to generation of pinholes there and thus troubles in reverse osmotic filtration. In addition, when the fabric is wound around a roll in the manufacturing process, the penetrated resin becomes in contact with the surface of the lower wound fabric, occasionally damaging the resin surface, and accordingly, the penetration of resin through the fabric is also undesirable from the viewpoint of quality control.

From the above, it can be understood that fine and uniform pore size is very significant for a support. There inevitably exists large pores in the cited reference invention, being basically different from the present invention and unable to be applied to high pressure filtration as the present invention.

Fig.1 Micropore distribution (differential) curve of nonwoven fabric A

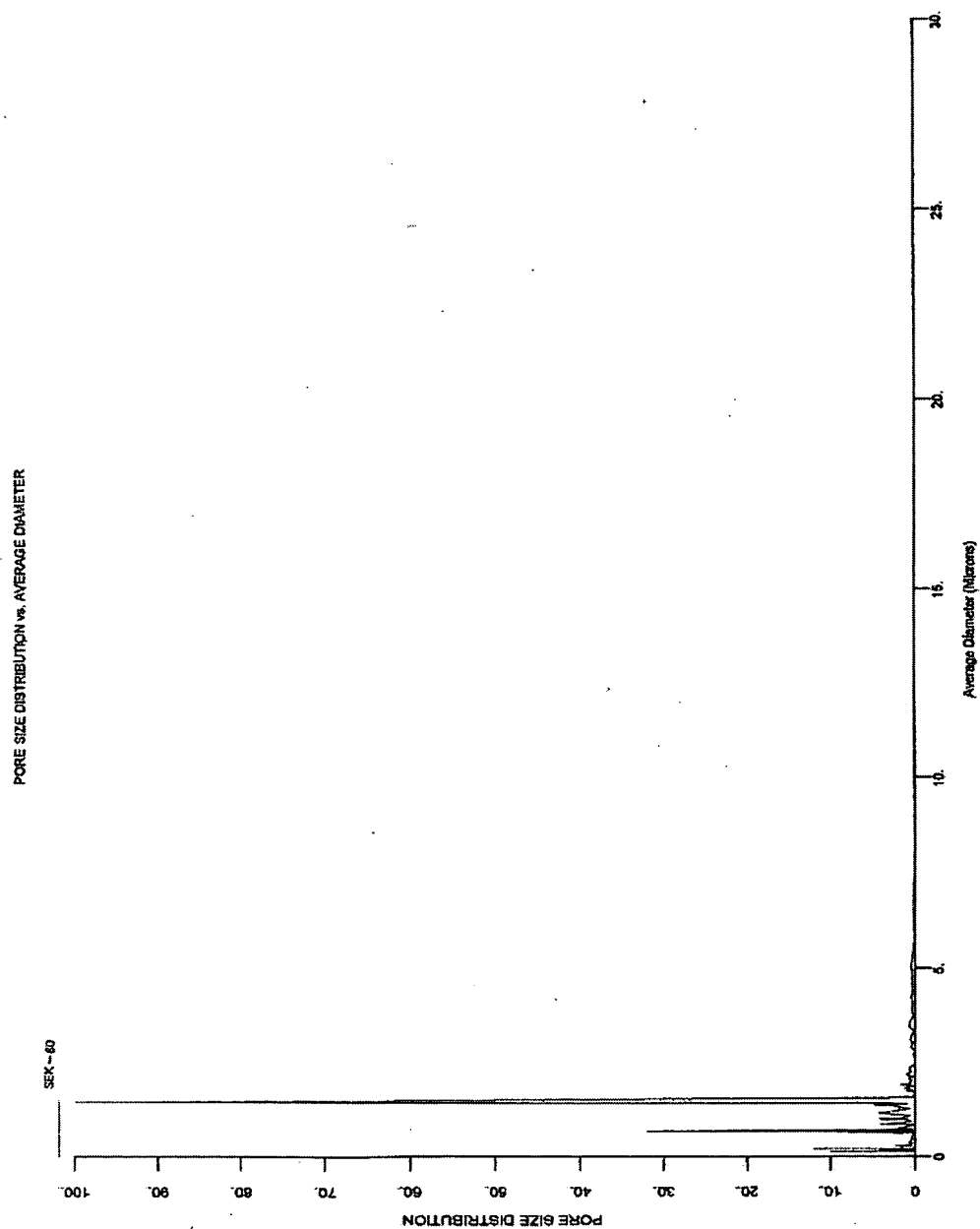


Fig. 2 Micropore distribution (histogram) of nonwoven fabric A

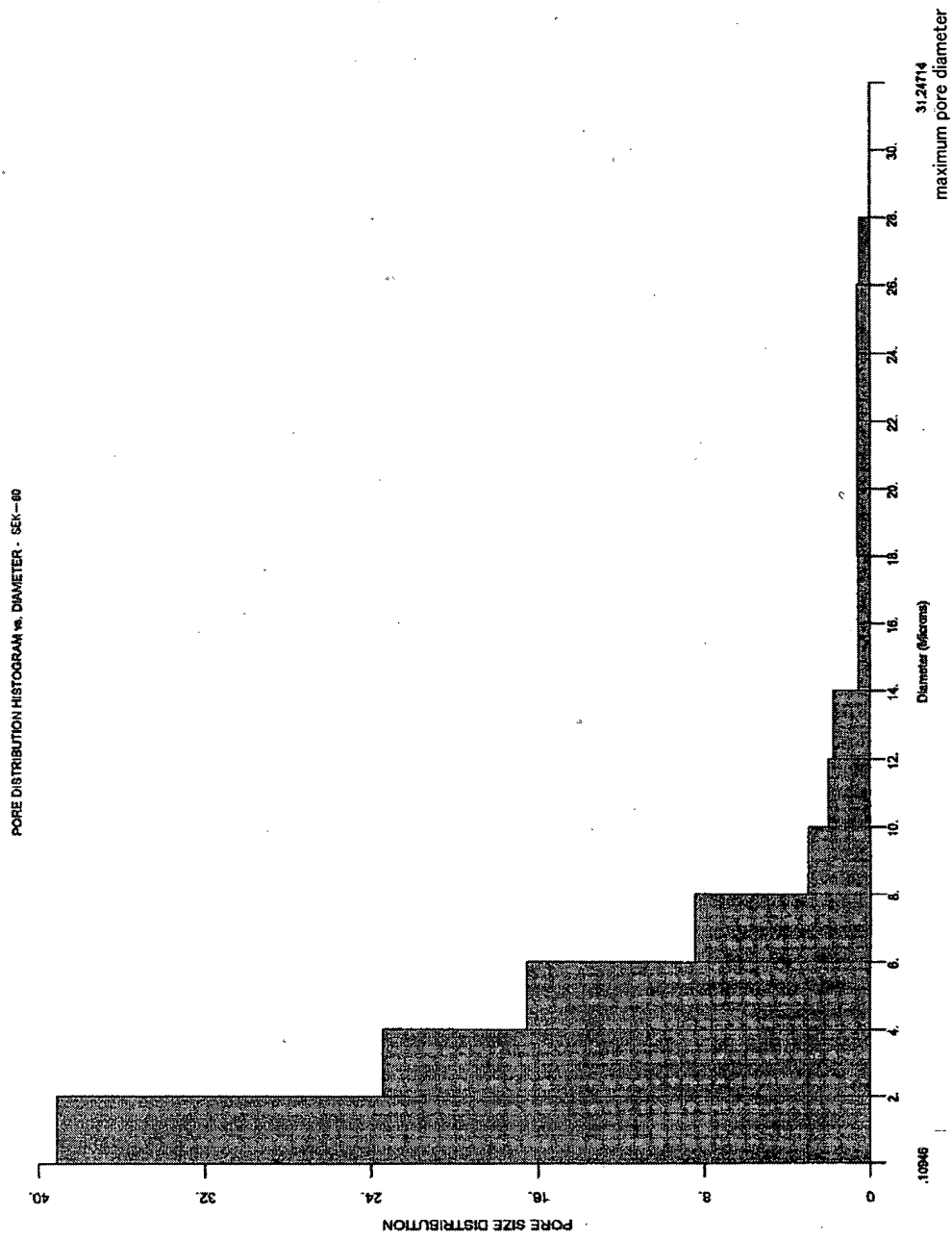


Fig. 3 Micropore distribution (differential) curve of nonwoven fabric B

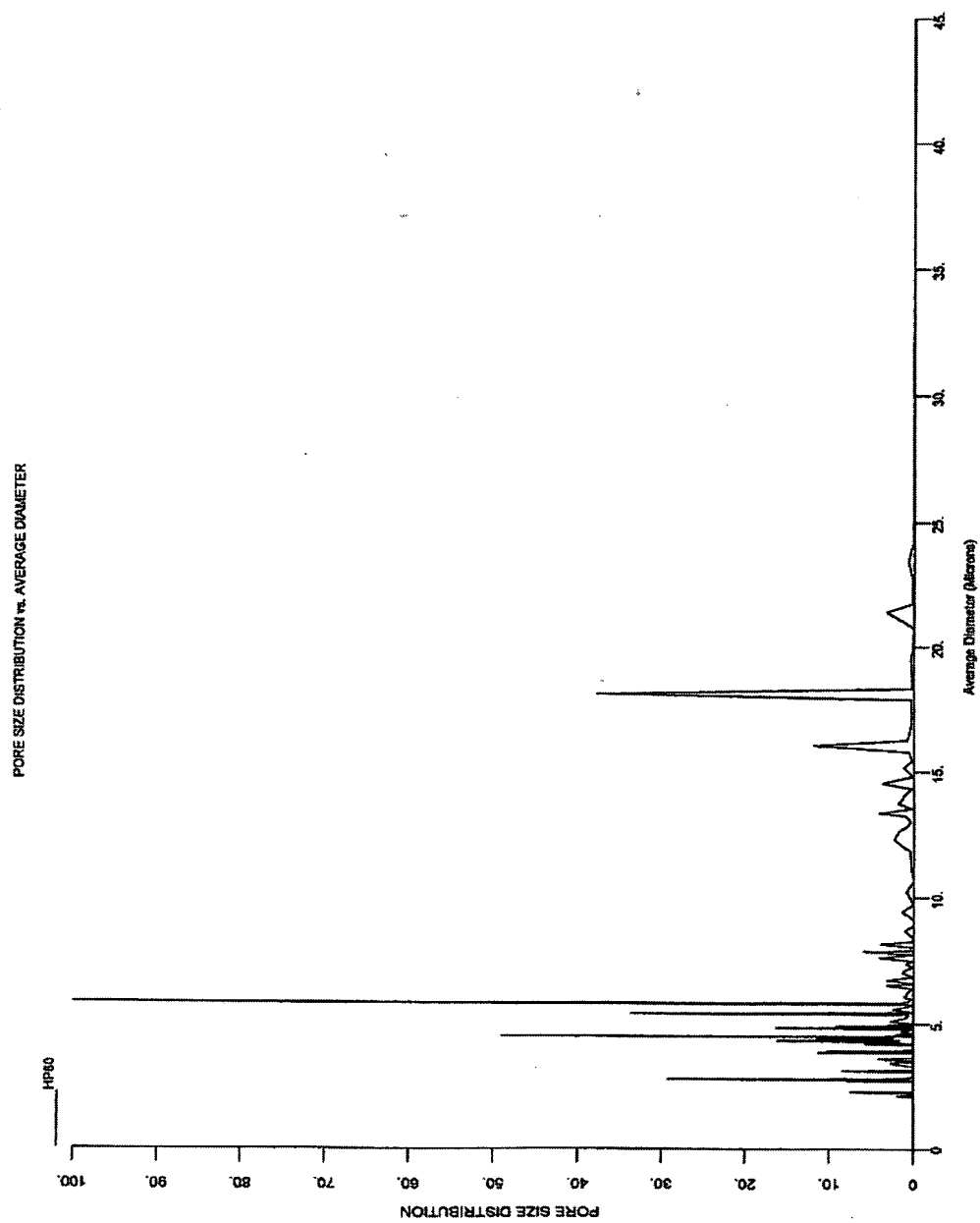


Fig.4 Micropore distribution (histogram) of nonwoven fabric B

